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(21) International Application Number: PCT/EP99/03367 (22) International Filing Date: 12 May 1999 (12.05.99) (30) Priority Data: 9810656.0 18 May 1998 (18.05.98) GB (71) Applicant (for AU BB CA CY GB GD GH GM IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB). (71) Applicant (for all designated States except AU BB CA CY GB GD GH GM IE IL IN KE LC LK LS MN MW NZ SD SG SL SZ TT UG US ZW): UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL). (71) Applicant (for IN only): HINDUSTAN LEVER LIMITED [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Mumbai 400 020, Maharashtra (IN). (72) Inventors; and (75) Inventors/Applicants (for US only): THORNTHWAITE, David, William [GB/GB]; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside L63 3JW (GB). WHALEY, Christopher [GB/GB]; Unilever		Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside L63 3JW (GB). (74) Agent: ELLIOTT, Peter, William; Unilever plc, Patent Dept., Colworth House, Sharnbrook, Bedford MK44 1LQ (GB). (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: STABLE QUATERNARY AMMONIUM COMPOSITIONS (57) Abstract The invention provides stable compositions comprising ester-containing quaternary ammonium material and one or more stabilising agent(s) chosen from: a) urea, b) urea derivatives, c) organic compounds with at least one free lone pair of electrons chosen from: i) primary amines, ii) secondary amines, and/or iii) tertiary amines, iv) glycerol wherein the composition is a liquid, molten or semi-solid containing 10 % or less water, and when glycerol is used the ammonium material has 2 or less CH ₃ groups attached to the quaternary nitrogen atom.		

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STABLE QUATERNARY AMMONIUM COMPOSITIONS

Technical field

5 The present invention relates to the stability of quaternary ammonium materials, in particular it relates to maintaining stable quaternary ammonium materials containing at least one ester group, in the raw material form or as a solution in a suitable solvent.

10

Background and prior art

Quaternary ammonium materials both solid or liquid are used extensively in fabric softener compositions. Typically such
15 compositions contain a water insoluble quaternary ammonium fabric softening agent dispersed in water at a level of quaternary ammonium softening agent up to 8% by weight in which case the compositions are considered dilute or at levels from 8 to 50% in which case the compositions are
20 considered concentrates.

The problem associated with quaternary ammonium materials containing at least one ester group is their instability on storage.

25

The problem is particularly noticeable in the storage of these materials at variable temperatures over time, especially at elevated temperatures eg in the region of 40-90°C, such as 50-85°C.

30

The instability of both such solid and liquid quaternary ammonium material may manifest itself by the discolouration of such material during storage at various temperatures.

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The amount of discolouration is generally an indication of the level of decomposition occurring over time. This decomposition is of greatest concern when quaternary ammonium material is stored at temperatures above their melting points.

Instability may also manifest itself by alkyl halide appearance in the sample, indicating decomposition of the quaternary ammonium material. Instability may be referred to as caused by, or indicated by, de-quaternisation of the quaternary ammonium material.

In the past, stability of quaternary ammonium compounds has been improved by the storage of compounds at low temperatures, i.e. temperatures well below the melting points of the compounds being stored. Also, the addition of anti-oxidants has been used to counteract decomposition.

EP 299 176 (Kao) discloses soft-finishing agents comprising a di-long chained quaternary ammonium salt containing a single ester group and a decyldimethyl amine.

EP 499 282 (Hoechst) discloses compositions comprising a quaternary ammonium compound and an aliphatic amine.

EP 332 270 (Unilever) discloses compositions comprising a quaternary ammonium fabric softening agent, an amine and an amphoteric material.

Surprisingly, we have found that low and high temperature stability of the aforementioned solid or liquid quaternary ammonium compounds may be improved by the addition of at

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least one stabilising agent selected from specific group of compounds which improve the stability of the composition.

Definition of the invention

5

Thus according to one aspect of the invention there are provided improved stable compositions comprising quaternary ammonium material materials containing at least one ester group characterised in that they further comprise one or
10 more stabilising agent(s) chosen from;

- a) urea
- b) urea derivatives
- c) one or more organic compounds having at least one free
15 lone pair of electrons chosen from;
 - i) primary amines RNH_2 , where R is a C_{3-17} alkyl, alkenyl, hydroxyalkyl or substituted derivative thereof,
 - ii) secondary amines, and/or
 - iii) tertiary amines $\text{NR}^1\text{R}^2\text{R}^3$ wherein $\text{R}^1\text{R}^2\text{R}^3$ are
20 independently C_1-C_{22} alkyl, alkenyl or hydroxyalkyl groups or substituted derivatives thereof, and wherein when both R^1 and R^2 are $-\text{CH}_2\text{CH}_2\text{OH}$ or both R^1 and R^2 are $-\text{CH}_2\text{CH}_2\text{OCOR}^4$, R^4CO is C_{16-18} , then R^3 is not a methyl group
- 25 iv) glycerol

with the proviso that the composition is in a liquid, molten or semi-solid form containing 10% or less water, and wherein when the stabilising agent is glycerol the quaternary
30 ammonium material has 2 or less methyl groups directly attached to the quaternary nitrogen atom.

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Such compositions show improved stability at varying temperatures.

5 In a second aspect of the present invention there is provided a process of stabilising quaternary ammonium material materials containing at least one ester group by the addition of one or more stabilising agents as defined above.

10 According to a further aspect of the invention is provided a solid rinse conditioner comprising a composition as defined above.

15 According to a further aspect of the invention is provided a liquid rinse conditioner made by dilution of a composition as defined above with water.

20 According to a further aspect of the invention is provided a method of reducing the alkyl halide levels in quaternary ammonium material materials containing at least one ester group over time by the addition of a stabilising as defined herein.

25 As used herein the term ester group in the ammonium material material includes an ester group which links two hydrocarbyl chains. References herein to ammonium material materials are to those having at least one ester group in their structure.

30 Detailed description of the invention

The quaternary ammonium materials containing at least one ester group of the invention preferably do not contain substantial amounts of non- ester containing material.

- 5 -

Preferably the ester containing quaternary ammonium material is used in the absence of non-ester group quaternary ammonium containing material. However where necessary small amounts eg less than 20% by weight based on the amount of
5 total quaternary ammonium material, preferably less than 10% may be present.

The invention is of application to quaternary ammonium materials containing at least one ester group, wherein at
10 least one higher molecular weight group and two or three lower molecular weight groups are linked to a common nitrogen atom to produce a cation and wherein the electrically balancing anion is a halide, acetate or lower alkylsulphate ion, such as chloride or methanesulphate.

15 The higher molecular weight substituent on the nitrogen is preferably a higher alkyl group, containing 12 to 28, preferably 12 to 22, such as 14 to 20 carbon atoms, such as coco-alkyl, tallowalkyl, hydrogenated tallowalkyl or
20 substituted higher alkyl. The lower molecular weight substituents are preferably lower alkyl of 1 to 4 carbon atoms, such as methyl or ethyl, or substituted lower alkyl. One or more of the said lower molecular weight substituents may include an aryl moiety or may be replaced by an aryl,
25 such as benzyl, phenyl or other suitable substituents. A preferred quaternary ammonium salt is a di-higher alkyl, di-lower alkyl ammonium halide.

Preferably the quaternary ammonium is a compound having two
30 C₁₂-C₂₂ alkyl or alkenyl groups connected to a quaternary ammonium head group via at least one ester link or a compound comprising a single long chain with an average

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chain length equal to or greater than C₂₀. Preferably there are two or more such ester linkages. More the quaternary ammonium material has two long chain alkyl or alkenyl chains with an average chain length equal to or greater than C₁₄.

5 Even more preferably each chain has an average chain length equal to or greater than C₁₆. Most preferably at least 50% of each long chain alkyl or alkenyl group has a chain length of C₁₈. It is preferred if the long chain alkenyl or alkenyl groups are predominantly linear.

10

It is especially preferred that the quaternary ammonium material contains two or more ester groups. In both the monoester and di-ester materials it is preferred that the ester group(s) are linking groups between a hydrocarbyl
15 chain, eg an alkyl chain, attached to the quaternary nitrogen atom and a further hydrocarbyl chain, eg an alkyl group.

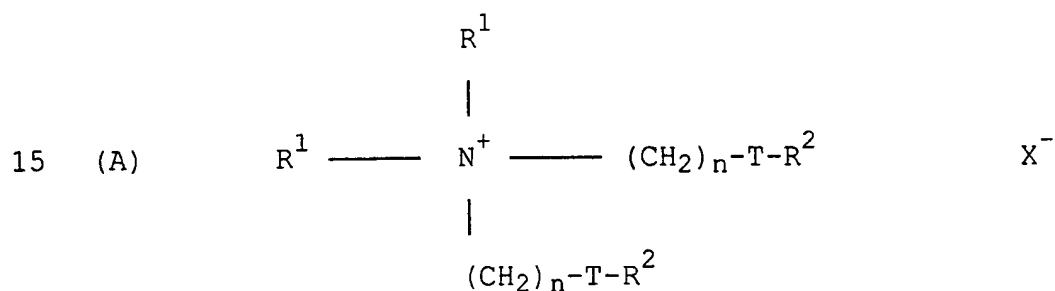
The problems identified above have especially been found to
20 be associated with quaternary ammonium materials with two or three electron withdrawing groups attached to the quaternary nitrogen atom through a hydrocarbyl (alkyl) chain of one or two carbon atoms, and, one or two short alkyl chains, (especially methyl) also directly attached to the nitrogen
25 atom. This arrangement is shown in formula (A) below.

Compounds of type A having two methyl groups and two electron withdrawing groups attached to the quaternary nitrogen atom through an alkyl chain of two carbon atoms are of particular application in the present invention. Such
30 compounds having a chloride counterion have been found to especially benefit from the present invention.

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It is believed that the problems identified above are most common in quaternary ammonium materials having an ester linking group and one or two methyl groups attached directly to the quaternary nitrogen atom, a chloride counterion, and
 5 two electron withdrawing groups separately linked to the quaternary nitrogen atom. The compounds of general formula A may suffer most from the problems identified above and are especially preferred according to the invention.

10 The especially preferred ester-linked quaternary ammonium material for use in the invention can be represented by the formula:



wherein each R^1 group is independently selected from C_{1-4} alkyl, hydroxyalkyl or C_{2-4} alkenyl groups; and wherein each
 20 R^2 group is independently selected from C_{8-28} alkyl or alkenyl groups; X^- is any suitable counterion, for instance a halide, acetate or lower alkosulphate ion, such as chloride or methosulphate.

25

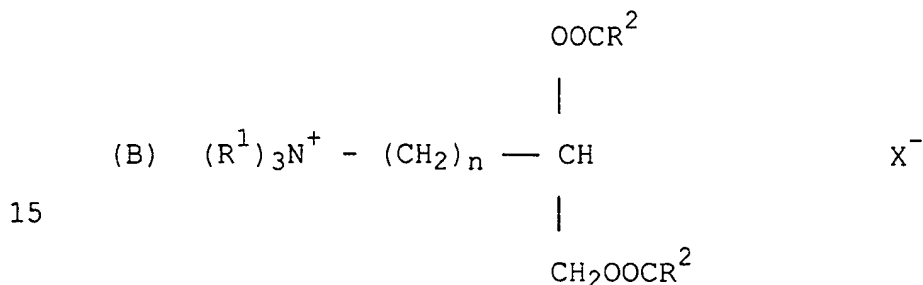
$$\begin{array}{cc}
 \text{O} & \text{O} \\
 || & || \\
 \text{T is } -\text{O}-\text{C}- & \text{or } -\text{C}-\text{O}-; \text{ and} \\
 n \text{ is an integer from } 1-5 \text{ or is } 0.
 \end{array}$$

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It is especially preferred that in compounds of type (A) each R^1 group is methyl and each n is 2. It is also preferred that where R^1 is methyl then R^2 is not ethanol.

- 5 Di(tallowyloxyethyl) dimethyl ammonium chloride, available from Hoechst, is especially preferred, also Di(hardened tallowyloxyethyl)dimethyl ammonium chloride, ex Hoechst).

Another preferred type of ester linked quaternary ammonium
10 material that can be used in the invention is represented by the formula:



wherein R^1 , n , R^2 and X^- are as defined above.

It is advantageous for environmental reasons if the quaternary ammonium material is biologically degradable.

20

Preferred materials of this class such as 1,2 bis[hardened tallowoyloxy]-3- trimethylammonium propane chloride and their method of preparation are, for example, described in US 4 137 180 (Lever Brothers). Preferably these materials
25 comprise small amounts of the corresponding monoester as described in US 4 137 180 for example 1-hardened tallowoyloxy-2-hydroxy -3-trimethylammonium propane chloride.

Accordingly it is especially preferred that the quaternary
30 ammonium compound according to the invention has at least one methyl group attached to the quaternary nitrogen atom and two or three nitrogen atom substituents containing

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electron withdrawing groups and a chloride counterion. It is especially preferred that such compounds falling within general formula A above are used and particularly that both R^1 groups are methyl and in the remaining radicals n is 1 or 2 and R^2 is $C_{12} - 22$, especially $C_{16} - 22$, eg Tallow.

It is also preferred that the quaternary ammonium compound used in the present invention is substantially anhydrous, meaning containing less than 10% water in the context of the present invention.

The quaternary ammonium material may contain optional additional components, as known in the art, in particular, low molecular weight solvents, for instance isopropanol and/or ethanol, and co-actives such as nonionic softeners, for example fatty acid or sorbitan esters.

Any of the above-mentioned stabilising agents may be used according to the invention.

The stabilising agent is preferably added to the composition of the present invention at levels of 0.05 to 10% by weight of the weight of the quaternary ammonium material, more preferably 0.5 to 8.5% and even more preferably 0.75 to 7.5%, eg 1 to 5%.

In the tertiary amine stabilising agents the $R^1R^2R^3$ substituents include $OCOR^4$ substituents wherein R^4 is a $C_{12} - C_{22}$ alkyl or alkenyl chain.

If glycerol is used as the stabilising agent then the quaternary ammonium material has 2 or less methyl groups directly attached to the quaternary nitrogen atom. A

- 10 -

combination of glycerol and a quaternary ammonium compound of general formula (A), especially DEQ, has been found to be advantageous.

- 5 The most preferred stabilising agents are urea and tertiary amines where R^1 and R^2 are $C_1 - C_2$ alkyl groups and R^3 is a $C_2 - C_4$ hydroxyalkyl group eg N,N-dimethyl ethanolamine (DMEA).

The stabilising agent may be introduced to the quaternary ammonium material at any stage during its manufacture or
10 after manufacture, eg on storage. The stabilising agent may be added in any form, as a powder direct to the molten quaternary ammonium material or as a solution in a suitable solvent, for instance isopropanol.

15

The addition of the stabilising agent can take place during the synthesis of the quaternary ammonium material preferably following the quaternisation step. The addition may alternatively, or additionally, be made during storage of
20 the quaternary ammonium material.

The stabilising agent is most effectively introduced at any stage following the quaternisation step of the synthesis of the quaternary ammonium material.

25

The composition is in a liquid, molten or semi molten form containing less than 10% by weight of water. These compositions may be incorporated into a solid rinse conditioner which is preferably in a powdered or granular
30 form. The compositions may also be diluted with water to produce a liquid rinse conditioner.

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Examples

The invention will now be illustrated by the following examples. Further examples within the scope of the present invention will be apparent to the skilled person in the art.

Example 1

Urea was added to the quaternary ammonium material as a powder and heated to 82°C. The combined material was stored for three days.

The reflectance was measured on a datacolor international Spectraflash SF600 plus reflectometer after 3 days storage at 82°C.

	R540 after 3 days at 82°C
DEQ (control)	19.8
DEQ + 3.6% urea	25.1
DEQ + 7.3% urea	27.4

DEQ is di(2-[hardened tallow]oxyl oxyethyl) dimethyl ammonium chloride ex Hoechst. It includes approximately 10% mono ester and minor amounts of unquaternised amine/amine salt as well as approximately 2% fatty acid and 14% isopropanol.

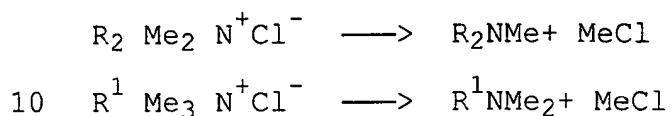
These results show that addition of urea to compositions comprising a quaternary ammonium compound counteracts decomposition at particularly high temperatures. This is indicated by the greatly increased R540 reflectance values found for samples of quaternary ammonium compound stored in admixture with urea.

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The following examples show the reduction in decomposition of the quaternary ammonium material by the reduction in liberation of alkyl halide on incorporation of a stabilising agent in accordance with the present invention.

5

Alkyl halide is produced by the following decomposition reaction:



where R is a C₈ to C₂₂ hydrocarbyl group, optionally interrupted by functional groups, e.g. ester [O-CO., CO.O], amide, ether, amine, carbonate), optionally branched,
15 optionally unsaturated and R¹ is a C₈ to C₄₀ hydrocarbyl group similarly defined.

Example 2

20 Urea was mixed with DEQ prior to heating at 82°C.

The chloromethane levels were determined by capillary gas chromatography.

Formulation	MeCl (ppm) after 3 days at 82°C
DEQ (control)	283
DEQ plus 3.6% urea	52
DEQ plus 7.3% urea	24

25

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DEQ is di(2-[hardened tallow]oxyl oxyethyl) dimethyl ammonium chloride ex Hoechst. It includes approximately 10% mono ester and minor amounts of unquaternised amine/amine salt as well as approximately 2% fatty acid and 14% isopropanol.

Example 3

DMEA was added to the DEQ following storage of the DEQ overnight at 82°C. Chloromethane was determined by gas chromatography after a further day at 82°C.

Formulation	MeCl (ppm) after storage at 82°C
DEQ (control)	80 (1 day)
DEQ plus 0.76% DMEA	32 (1 day)
DEQ plus 2.28% DMEA	5 (30 minutes)
DEQ plus 2.28% DMEA	2 (1 day)

DMEA is N,N-dimethylethanol amine (99% ex Aldrich)

All examples above demonstrate that the addition of DMEA reduces the level of methyl chloride generation over time in quaternary ammonium material stored at high temperatures. The level of decomposition is reduced thus resulting in more stable quaternary ammonium material. Furthermore the result after 30 minutes for the addition of DMEA shows the rapid and excellent effect thereof upon the level of methyl chloride.

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Example 4

Glycerol was added at a level of 7.5% by weight to a sample of DEQ to produce example 4A. A control sample of DEQ which
5 did not contain any glycerol (Comparative example 4B) and example 4A were sealed in separate Gas Chromatograph (GC) vials and were stored at 80.5°C. At the end of the storage period the level of 'total' methyl chloride in each sample was measured. The results are given below.

10

Example	'Total' MeCl (ppm) after 9 days storage at 80.5°C.
4A	173
4B (comparative)	378

The above results demonstrate the ability of the stabilising agent, here glycerol, to reduce the level of MeCl in a quaternary ammonium material on closed, high temperature,
15 storage. The level of MeCl measured here is the 'total' level in a sealed system.

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CLAIMS

1. Stable compositions comprising quaternary ammonium
material materials containing at least one ester group
5 characterised in that they further comprise one or more
stabilising agent(s) chosen from;
- a) urea
 - b) urea derivatives
 - c) one or more organic compounds having at least one
10 free lone pair of electrons chosen from;
 - i) primary amines RNH_2 , where R is a C_3 - 17 alkyl,
alkenyl, hydroxyalkyl or substituted derivative
thereof,
 - ii) secondary amines, and/or
 - 15 iii) tertiary amines $\text{NR}^1\text{R}^2\text{R}^3$ wherein $\text{R}^1\text{R}^2\text{R}^3$ are
independently C_1 - C_{22} alkyl, alkenyl or hydroxyalkyl
groups or substituted derivatives thereof, and
wherein when both R^1 and R^2 are $-\text{CH}_2\text{CH}_2\text{OH}$ or both
 R^1 and R^2 are $-\text{CH}_2\text{CH}_2\text{OCOR}^4$, R^4CO is C_{16-18} , then R^3
20 is not a methyl group
 - iv) glycerol
- with the proviso that the composition is in a liquid,
molten or semi-solid form containing 10% or less water,
and wherein when the stabilising agent is glycerol the
25 quaternary ammonium material has 2 or less methyl groups
directly attached to the quaternary nitrogen atom.

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2. A composition according to claim 1 wherein the stabilising agent is urea or a tertiary amine wherein R^1 and R^2 are C_1 - C_2 alkyl groups and R^3 is a C_2 - C_4 hydroxyalkyl, preferably N-N-dimethyl ethanolamine.

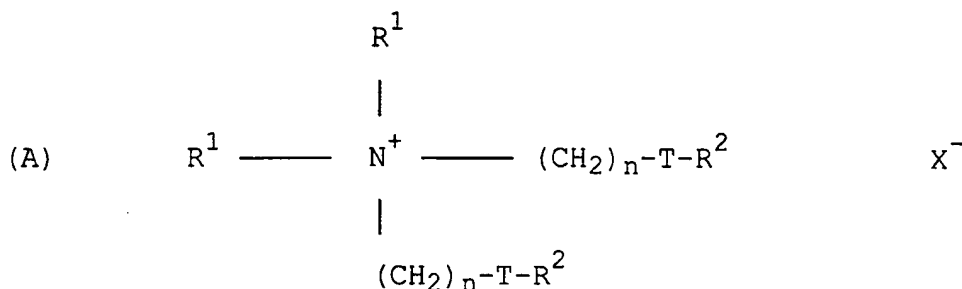
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3. A composition according to any one of the preceding claims where the stabilising agent is present at levels of 0.05 to 10% by weight of the weight of the quaternary ammonium material, preferably 0.5 to 8.5%, even more preferably 0.75 to 5%.

10

4. A composition according to any one of the preceding claims wherein the quaternary ammonium material is of formula

15



20

where each R^1 group is independently selected from C_1 -4 alkyl, hydroxyalkyl or C_2 -4 alkenyl groups; and each R^2 group is independently selected from C_8 -28 alkyl or alkenyl groups; X^- is any suitable counterion,

25

$$\begin{array}{cc} O & O \\ || & || \end{array}$$

T is -O-C- or -C-O-; and
n is an integer from 1-5 or is 0.

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5. A composition according to claim 4 wherein where each R^1 group is methyl, each R^2 group is tallow, X^- is chloride and n is 2.
- 5 6. A process of stabilising quaternary ammonium material containing at least one ester group via the steps of adding at least one stabilising agent of claim 1 to the quaternary ammonium material.
- 10 7. Process according to claim 6 wherein addition of the stabilising agent occurs during the manufacture of the quaternary ammonium material, preferably following the quaternisation step in the synthesis of the quaternary ammonium material.
- 15 8. Process according to either claim 6 or claim 7 wherein addition of the stabilising agent occurs after manufacture of the quaternary ammonium material, preferably during storage thereof.
- 20 9. A solid rinse conditioner comprising a composition as defined in any of claims 1-5, preferably in granular or powdered form.
- 25 10. A liquid rinse conditioner made by dilution of a composition as defined in any of claims 1-5, with water.
- 30 11. Method of reducing the alkyl halide levels in quaternary ammonium material containing at least one ester group over time by the addition of a stabilising agent as defined in claim 1.

INTERNATIONAL SEARCH REPORT

International Application No

PC 1/EP 99/03367

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D1/62 C11D3/32 C11D3/20 C11D3/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D D06M B01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 543 067 A (PHAN DEAN V ET AL) 6 August 1996 (1996-08-06) claims 1-13, 23, 25, 30 examples ---	1, 3-6, 8, 11
A	US 5 282 983 A (NISHIMOTO UICHIRO ET AL) 1 February 1994 (1994-02-01) claims column 7, line 37 - line 46 ---	1-3, 6-11
A	DE 24 54 465 A (HOECHST AG) 20 May 1976 (1976-05-20) claims 1, 2 page 1, paragraph 2 --- -/--	1, 2, 6, 8, 9, 11

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 196 29 666 A (HENKEL KGAA) 29 January 1998 (1998-01-29) claims 1-5 examples ----	1,3-6,8, 11
A	DE 43 07 186 A (HENKEL KGAA) 15 September 1994 (1994-09-15) claims examples 4-7 page 2, line 8 - line 17 ----	1,3,6,8, 10
A	EP 0 332 270 A (UNILEVER) 13 September 1989 (1989-09-13) cited in the application claims 1,3,4,8 example 10 page 5, line 3 - line 54 ----	1-6,8-11
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A	US 4 851 138 A (JAROSCHEK HANS-JOACHIM ET AL) 25 July 1989 (1989-07-25) claims 1,5,8-11 column 3, line 32 -column 4, line 11 -----	1,2,6,8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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